



## Performance of Titanate Ceramics for Plutonium Disposition

The Department of Energy has selected a two-pronged approach for the disposition of up to 50 metric tons of surplus plutonium. Approximately 13 metric tons will be immobilized in a titanate ceramic; the balance will be fabricated into a mixed oxide fuel and irradiated in commercial light water reactors. Members of the Chemical Technology Division are conducting research to support qualification of the ceramic waste form for disposal in the proposed high-level waste repository at Yucca Mountain.

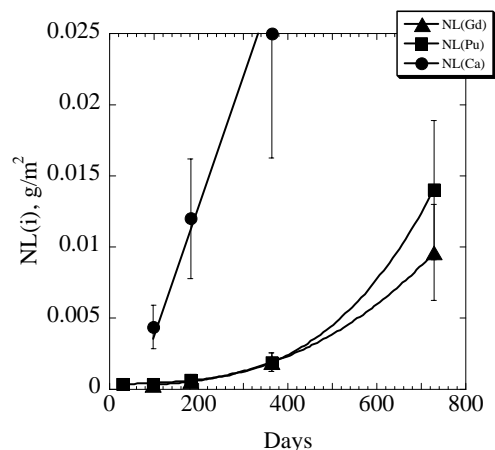
Part of this qualification effort is to understand the microstructure of the ceramic, and then relate the corrosion behavior of the ceramic to the microstructure. Phases that are typically present in the ceramic include pyrochlore  $[(\text{Ca}, \text{Gd}, \text{Pu})(\text{Hf}, \text{Pu}, \text{U}, \text{Gd})\text{Ti}_2\text{O}_7]$ , the related phase zirconolite, Hf-bearing rutile  $[(\text{Ti}, \text{Hf})\text{O}_2]$ , brannerite  $[(\text{U}, \text{Pu}, \text{Gd})\text{Ti}_2\text{O}_6]$ , and minor amounts of  $\text{PuO}_2$ . A state-of-the-art scanning electron microscope is used to characterize the ceramic.

As part of the testing program, a series of corrosion tests with crushed ceramic (100-125  $\mu\text{m}$ ) was completed over a two-year period. The release rates of Pu and Gd from a titanate ceramic during corrosion tests increased rapidly after one year of reaction (see figure). In contrast, the release of Ca increased linearly. Four possible processes could explain the increasing release rates of Pu and Gd:

- Release of colloids from the waste form might lead to an increase in the measured concentrations of Pu and Gd. The colloids observed in leachates appeared to be small pieces of ceramic. If the colloids were responsible for the increased Gd and Pu releases, then Al, Ca, Ba, Zr, and Ti release would also increase. Since this was not

observed, colloids were probably not responsible for the Gd and Pu behavior.

- Precipitation of solids during testing would decrease the concentration of important elements in solution, possibly leading to an increase in the corrosion rate. However, few precipitates were observed on the reacted ceramic, and they seldom contained major ceramic elements.
- An increase in surface area during tests could have served to increase corrosion. If the surface area increased, then the release rates of all elements would increase. Because this is not observed, an increase in reactive surface area does not adequately explain the observed Gd and Pu release.



*Normalized Mass Losses,  $NL(i)$ , for the Zirconolite-1 Ceramic as a Function of Time*

- Dissolution of a less-durable phase is the most likely explanation for the increasing Pu and Gd release. Previous results showed that brannerite dissolves faster than other titanate phases, and brannerite contains both Pu and Gd.

Particles of the ceramic recovered from the two-year corrosion test were examined with scanning electron microscopy. In particular, we were interested in any changes in the brannerite during the test. In the unreacted ceramic, brannerite is surrounded by  $\text{PuO}_2$  (figure below, left). In the reacted ceramic, voids surrounded  $\text{PuO}_2$  (figure below, right); little brannerite was found in the reacted sample.

This absence of brannerite in reacted ceramics is consistent with the Pu and Gd release behavior in these same tests. If the Pu- and Gd-bearing brannerite dissolves faster than any of the other phases in this ceramic, then Pu and Gd would be released at a higher rate than Ca.

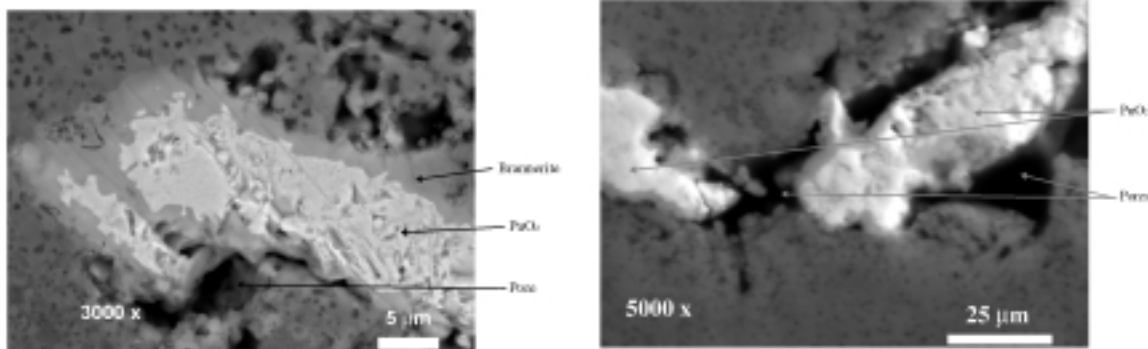
The apparent increase in the dissolution rate of brannerite with increasing test duration is somewhat difficult to explain. One possible explanation is that the reacting surface area of the ceramic increased as

test duration increased. As a brannerite grain dissolved, voids would have been generated. These voids could have enlarged and connected existing pores. Development of interconnected porosity would have allowed water to move more freely through the ceramic and provided access to a larger surface area of brannerite.

In sum, the dissolution of one phase, brannerite, was shown to control the release of Pu and Gd from this titanate ceramic. On the basis of this conclusion, the absence of brannerite in the final immobilization ceramic would lead to significantly lower Pu and Gd releases. Therefore, we have recommended that steps be taken in the fabrication procedure to minimize the amount of brannerite in the final immobilization ceramic.

## ANL Participants

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*Scanning Electron Micrographs of Unreacted Titanate Ceramic Showing Brannerite Surrounding  $\text{PuO}_2$  (left) and Particle of the Same Ceramic after Two Years of Corrosion under Product Consistency Test-B Conditions. Note voids surrounding the  $\text{PuO}_2$  (right).*